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Gas Chromatography of Zinc Pivaloyltrifluoroacetonate Adducts with Tri-n-Butylphosphate and Tri-n-Butylphosphine Oxide

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The detection of mixed-ligand complexes of zinc by gas chromatography was reported. Pivaloyltrifluoroacetone was used in combination with organic neutral ligands such as tri-*n*-butylphosphate and tri-*n*-butylphosphine oxide to extract zinc ion synergistically as mixed ligand complexes which were volatile and thermally stable. The composition of the extracted species was considered to be $Zn(PTA)_2 \cdot L$. Analytical curves were prepared and found usable through a range of 2 to 30 μg zinc.

INTRODUCTION

The gas chromatograms of the metal chelates of such fluorinated β-diketones as 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione[1] and pivaloyltrifluoroacetone[2,3] were successfully obtained. Recently, the gas chromatography of β-diketone adducts with some organophosphorus compounds has been reported.[4~7] The method is expected to have the advantages that non-volatile or unstable chelates are changed into volatile or more stable chelates by adduct formation and that the synergistic extraction caused by the adduct formation produces high extractability of an aiming metal. Zinc β-diketonates are very difficult to be eluted. In this paper we would like to describe the gas chromatography of the adducts of zinc pivaloyltrifluoroacetone chelate with tri-*n*-butylphosphate and tri-*n*-butylphosphine oxide.

EXPERIMENTAL

Reagents

Pivaloyltrifluoroacetone (HPTA) was synthesized by the Claisen condensation[8] of pinacoline and ethyl trifluoroacetate with sodium methoxide or was purchased from the Dojindo Co., Ltd., Research Laboratories. Such neutral bases as tri-*n*-butylphosphine oxide (TBPO), tri-*n*-octylphosphine oxide (TOPO) and tri-*n*-butylphosphate (TBP) were obtained commercially and were used without further purification.

The radioisotope, zinc-65 was supplied by New England Nuclear, Boston, Mass., U. S. A., as chloride in hydrochloric acid.

All the other reagents were GR grade materials.

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Apparatus

Gas chromatograms were obtained with Yanagimoto gas chromatograph G-80 equipped with a thermal conductivity detector. Chromosorb W AW DMCS (80–100 mesh) coated with 3 per cent (by weight) Silicone OV-101 was packed into a glass column (75 cm × 3 mm i.d.). The injection temperature was kept at 270°C, the column was programmed from 150 to 240°C at various rates, and the detector temperature was 280°C. Helium was used as the carrier gas.

Solvent Extraction Procedure

Zinc stock solution was prepared by dissolving the dry zinc oxide with hydrochloric acid, evaporating to near dryness, and diluting it with pure water. For the investigation of the synergistic extraction of the zinc PTA chelate with neutral bases, the following procedure was adopted. Ten milliliters of an aqueous solution containing zinc with radioactivities, sodium perchlorate (0.10 M) and acetic acid (0.01 M) in a 30 ml glass stoppered centrifuge tube were adjusted to a desired pH and were shaken with 10 ml of benzene containing 0.05 M of HPTA and 10^{-3} M of the neutral base for 30 minutes. Centrifugation was used for separating the organic phase from the aqueous phase. Percent extraction or distribution ratio was obtained by counting the γ-activities with a NaI(Tl) scintillation counter.

Samples for gas chromatogram measurements were prepared by shaking 2.0 ml of aqueous solutions of zinc with 2.0 ml of benzene which contained HPTA in an amount 5 times the zinc concentration and neutral base in an amount 2 times the zinc concentration. After centrifugal separation, the gas chromatographic samples were injected by syringe directly from the organic phase of the extraction solutions.

RESULTS AND DISCUSSION

Gas Chromatography

Gas chromatograms of HPTA and neutral base mixed-ligand chelates of zinc were obtained. A typical chromatogram of the benzene phase of the extraction of zinc with HPTA and TBP is shown in Fig. 1. Figure 2 is a gas chromatogram of the zinc PTA adduct with TBPO. The excess HPTA was eluted with benzene in both cases. The examination of the glass inlet liner and the column packing in these systems gave no visual evidence of decomposition for any of the complexes, nor were spurious peaks observed in any of the chromatograms. These mixed-ligand chelates apparently had a thermal stability, while a parent zinc PTA chelate lacked a thermal stability and was not chromatographed without decomposition. In such mixed-ligand systems as $Zn(PTA)_2TOPO$, $Zn(DPM)_2TBP$, $Zn(DPM)_2TBPO$, $Zn(TAA)_2TBP$, $Zn(TAA)_2$-γ-picoline and $Zn(TAA)_2\alpha$-α'dipyridyl (where DPM=dipivaloylmethane and TAA=trifluoroacetylacetone), gas chromatograms were not obtained without decomposition or very broad and distorted chromatographic peaks were obtained.

Calibration curves were prepared for zinc chelate adduct with TBP. Reproducible linear relationship was obtained between the peak area and the amount of zinc in the range of 2 to 30 μg as shown in Fig. 3. It is necessary to confirm whether the metal chelate was eluted from gas chromatograph. Sample collection of the eluted species prior to identification was accomplished with a 10 cm length of 4 mm (in bore)

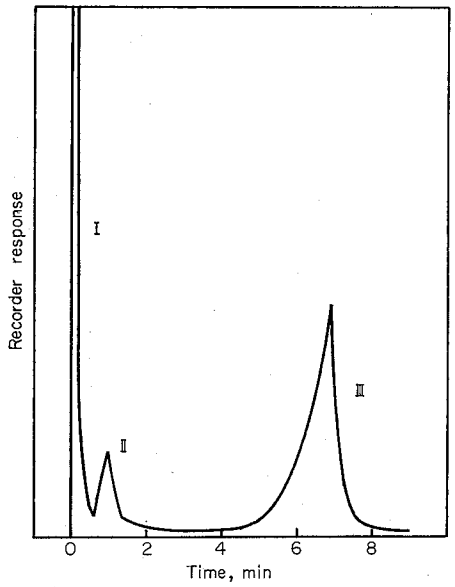

Fig. 1. Gas chromatogram for mixed ligand complex of zinc with HPTA and TBP
Column; 75 cm × 3 mm glass column, column packing; 3.0% Silicone OV-101 on Chromosorb W AW DMCS (80–100 mesh), column temp.; programmed from 150 to 240°C at 10°C/min, injection temp.; 270°C, TCD; 280°C, helium flow rate; 30ml/min.
I; Benzene, II; TBP, III; $Zn(PTA)_2$·TBP

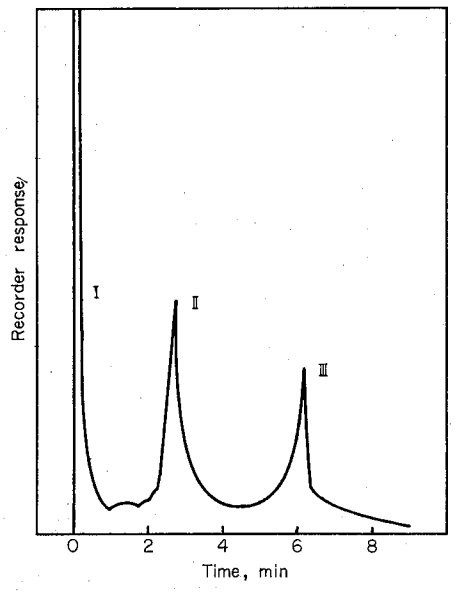

Fig. 2. Gas chromatogram of zinc PTA adduct with TBPO
Column temp.; programmed from 170 to 240°C at 10°C/min.
I; Benzene, II; TBPO, III; $Zn(PTA)_2$·TBPO
Others are same to in Fig. 1.

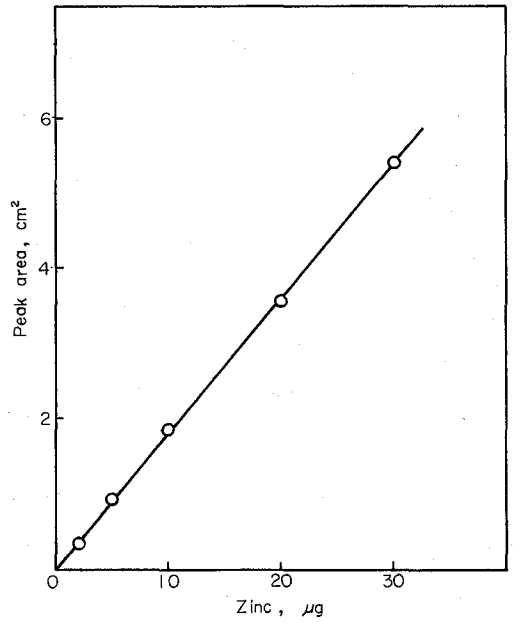

Fig. 3. Calibration curve for the mixed ligand complex of zinc with HPTA and TBP in the range from 2.0 μg to 30 μg metal
Column; 75 cm × 3 mm glass column, column packing; 3% Silicone OV-101 on Chromosorb W AW DMCS, column temp.; 200°C, TCD; 280°C and 100 mA, inlet temp.; 240°C, helium flow rate; 30 ml/min.

glass tube attached to the exit part. The collected samples were decomposed and washed out with hydrochloric acid and were ashed with perchloric acid. The existence of zinc was recognized spectrophotometrically by extracting the zinc ion in the ashed sample as dithizonate into chloroform.

Solvent Extraction

It is well known that some metal β-diketone chelates can often be extracted at a lower pH region by adding a suitable neutral ligand to the extraction system.[9] In the present system, the synergistic enhancement of the zinc extraction was also observed as shown in Fig. 4. Curves in Fig. 4 show the D *vs.* pH plots on the zinc extraction with HPTA in the absence or in the presence of a neutral ligand, where D is the distribution ratio and is calculated by the equation,

$$D = \frac{\gamma\text{-count rate per ml of the organic phase}}{\gamma\text{-count rate per ml of the aqueous phase}} \quad (1)$$

Each curve in Fig. 4 has an almost straight line with a slope of theoretical value, 2, when the HPTA concentration is kept constant. The ratio of HPTA to zinc is indicated as two from the slopes of the curves. In the presence of 10^{-3} M benzene solution of the neutral ligand, the extraction of zinc is enhanced in the following order; TBP<TBPO≃TOPO.

In the previous paper[10] the effect of the monodentate and bidentate neutral ligands acting as a synergist on the extraction of zinc with HPTA was investigated, in which

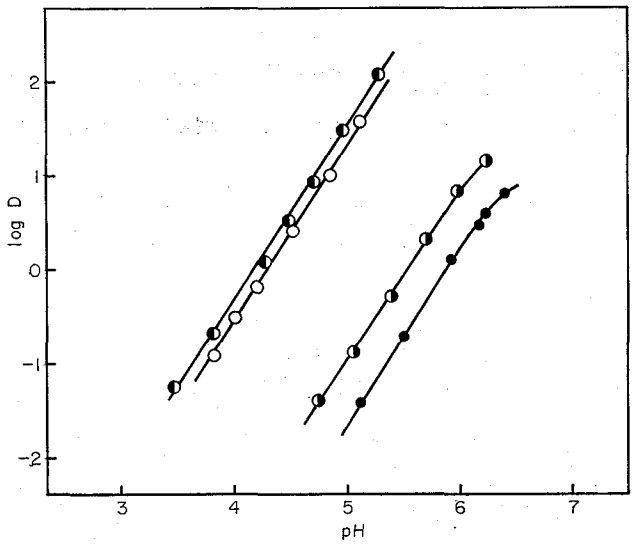

Fig. 4. Logarithm of the distribution ratio of zinc as a function of the pH value
Solvent; benzene, HPTA; 5×10^{-2} M, Molarity of added neutral ligand: -●-; none, -◑-; 10^{-3} M TBP, -○-; 10^{-3} M TBPO, -◐-; 10^{-3} M TOPO.

it was found that TOPO and its analogue reacted with the zinc PTA chelate to form 1 : 1 adduct as follows,

$$Zn(PTA)_2(org)+L(org)=Zn(PTA)_2L(org) \quad (2)$$

$$\beta=[Zn(PTA)_2L]_{org}/[Zn(PTA)_2]_{org}[L]_{org} \quad (3)$$

where L denotes the neutral ligand and β represents the stability constant of 1 : 1 adduct in the organic phase. As the 1 : 1 adduct with TOPO has such a high stability constant as $10^{6.19}$ in benzene, the concentration of bis complex of zinc is extremely small compared to the concentration of the mixed ligand chelates. Therefore, the species eluted from gas chromatograph is supposed to be $Zn(PTA)_2L$.

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